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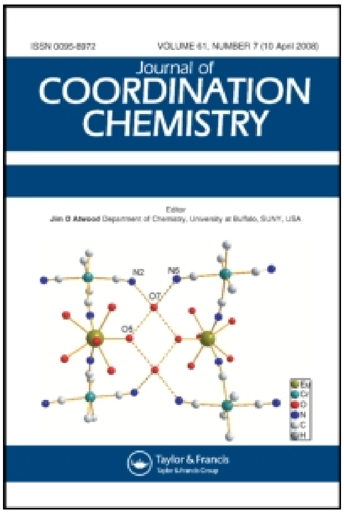

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SPECTROSCOPIC INVESTIGATION ON THE TRICHLORO-, TETRAHALO- AND MIXED-TETRAHALO-CUPRATES OF THE PIPERIDINIUM AND MORPHOLINIUM CATIONS

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SPECTROSCOPIC INVESTIGATION ON THE TRICHLORO-, TETRAHALO- AND MIXED-TETRAHALO-CUPRATES OF THE PIPERIDINIUM AND MORPHOLINIUM CATIONS

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Some halo- and mixed-halo-cuprates of the type $CuCl_3 \cdot L$, $CuCl_4 \cdot L_2$, $CuCl_3Br \cdot L_2$, $CuCl_2Br_2 \cdot L_2$ and $CuBr_4 \cdot L_2$, were prepared and characterized by means of far-i.r., i.r. and n.i.r. spectroscopy, magnetic moments and conductivity measurements. A band at 19000 cm^{-1}, which appears only in the $CuCl_3 \cdot L$ complexes, is characteristic of $Cu_2Cl_6^{2-}$ dimer or polymer species. For these complexes and for $CuCl_4(Morph)_2$ and $CuCl_3Br(Morph)_2$ (Morph = morpholinium cation) an approaching square-planar geometry, while for all the other complexes a distorted-tetrahedral geometry, may be suggested from their spectroscopic properties, compared to those of other tri- and tetra-halo-cuprates of known structure. An intermediate structure between these geometries may be proposed for the $CuCl_3 \cdot Pipd$ complex. The planar geometry is probably stabilized by extensive NH · · · Cl hydrogen bonding interactions greater with the morpholinium cation than with the piperidinium cation. No thermochromic behaviour in the solid state in the 290–370°K temperature range is observed. The room-temperature magnetic moments agree with the proposed configurations.

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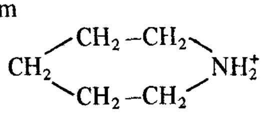
INTRODUCTION

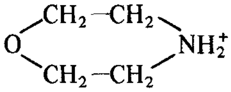
The work reported here is an outgrowth of a study of coordination compounds of substances such as piperazine, piperidine and morpholine, which are of great importance. Not only are they of interest as biologically active materials, but also their ring occurs as a constituent in many complex organic compounds which are of practical importance.

While many transition metal complexes of these ligands (1,2) have already been synthesized and investigated, no report has been found on the chemical behaviour of their hydrohalide salts in the presence of transition metal halides. This lack, the possibility of preparing very simple halo- and mixed-halo-metallates, and the great interest in the structural and electronic properties of copper halide complexes, have led us to extend our investigation with the study of the complexes formed between the piperidinium and morpholinium cations (hereafter abbreviated Pipd and Morph, respectively) and the copper halides.

The aliphatic heterocyclic amine cations, as piperidinium



and morpholinium



cations, assume a further interest, as, although they have nearly identical dimensions, the hydrogen bonding abilities, which are recognized as very important in causing the $CuCl_4^{2-}$ geometry (3,4), are different.

EXPERIMENTAL

Preparation of the Piperidinium and Morpholinium salts.

The salts were prepared by adding drop by drop a concentrated hydrogen halide solution to a concentrated ethanolic solution of the amine on ice-bath until a complete neutralization of the amine was reached. After concentration of the reaction solutions while compounds, recrystallized from absolute ethanol, precipitated.

Preparation of the Complexes

Dark red brown crystals of $CuCl_3 \cdot L$ were obtained by evaporation to near dryness of an ethanolic solution containing copper and ligand chloride. A molar excess of copper chloride was used to prevent formation of $CuCl_4 \cdot L_2$.

For the other complexes, in general, the method consists of mixing stoichiometric amounts of the appropriate amine hydrohalide and $CuX_2 \cdot 2H_2O$ (X = Cl and Br) in absolute ethanolic or methanolic solution and allowing the solution to cool or adding ethyl ether until precipitation occurs.

Physical Measurements

The electronic spectra of the solid compounds were recorded on a Beckman DK 1A spectrophotometer in the temperature range of 290–370°K. Samples were prepared by grinding the complexes on a filter paper as support. The infrared spectra of KBr pellets were recorded with a Perkin–Elmer 521 (4000–250 cm^{-1}) and the far-infrared spectra of nujol mulls with a Perkin–Elmer FIS3 (400–60 cm^{-1}) spectrophotometer. The room-temperature magnetic moments were measured with the Gouy method by using $HgCo(NCS)_4$ or $Ni(en)_3S_2O_3$ as calibrants and correcting for diamagnetism with the appropriate Pascal constants. The conductivities of the complexes in absolute ethanol (EtOH) or N,N′-dimethylformamide (DMF) solution were measured with a WTW (Wissen schaftlich-Technische Werkstätten) D812 Conductivity-Meter LBR at 25°C.

RESULTS AND DISCUSSION

The analytical results are reported in Table I. All the compounds are well-crystallized and stable in air.

Electronic Spectra and Magnetic Moments

There is considerable similarity between the room-temperature electronic spectra (Table II) of the $CuCl_3 \cdot L$, $CuCl_4(Morph)_2$ and $CuCl_3Br(Morph)_2$ complexes and those obtained for the $Cu_2Cl_6^{2-}$ dimers and for the approaching square-planar $CuCl_4^{2-}$ ion (5,6). While the position of the d-d bands does not change during transition from the square-planar monomeric species to the dimer, there being no strong perturbation of the electronic environment involved in the formation of the dimer, a new band appears at 19000 cm^{-1} only in the latter. This band, noted in $Cu_2Cl_6^{2-}$ dimers (5,6) and in $CsCuCl_3$ polymer (7,8), also appears in our $CuCl_3 \cdot L$ complexes and probably is a polarized charge-transfer

TABLE I
Analytical results

	Color	C% calcd	found	H% calcd	found	N% calcd	found	X% calcd	found	M.P. °C	μeff B.M.	λM EtOH	DMF
$CuCl_3 \cdot$ Pipd	red	23.44	24.15	4.72	4.73	5.47	5.39	41.55	40.94	155–59	2.02	43	67
$CuCl_4(Pipd)_2$	yellow	31.78	31.92	6.41	6.60	7.42	7.09	37.56	37.10	137–140	1.99	69	84
$CuCl_3Br(Pipd)_2$	red	28.43	28.95	5.73	6.07	6.64	6.60	44.14	44.11	141–145	1.88	72	115
$CuCl_2Br_2(Pipd)_2$	red	15.20	14.86	5.19	5.35	6.01	5.85	49.46	49.33	127–30	1.90	76	150
$CuBr_4(Pipd)_2$	red-violet	21.61	21.66	4.36	4.34	5.04	4.26	57.55	57.18	119–122	1.88	79	151
$CuCl_3 \cdot$ Morph	red	18.60	18.68	3.91	3.99	5.43	5.28	41.23	41.30	175–79	1.78	43	60
$CuCl_4(Morph)_2$	green	25.16	25.26	5.28	5.29	7.34	8.18	37.17	36.90	159–62	1.87	65	81
$CuCl_3Br(Morph)_2$	red	22.53	23.07	4.73	5.42	7.51	7.39	43.73	43.91	146–150	1.88	67	101
$CuCl_2Br_2(Morph)_2$	red	20.41	20.94	4.29	4.56	5.96	5.91	49.07	49.62	143–47	1.82	71	122
$CuBr_4(Morph)_2$	red-violet	17.16	17.16	3.60	3.54	5.00	4.47	57.15	57.13	126–30	1.77	75	144

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TABLE II
Electronic spectra in the solid state of the tetrahalo-and mixed-tetrahalo-cuprates (cm^{-1}).

	Ligand bands[1]					d-d bands			Charge-transfer bands			
$CuCl_3$ · Pipd	4270	4710	5180				10870		19050sh	24100sh		
$CuCl_4(Pipd)_2$	4350sh	4760sh				6620		9710	25000			
$CuCl_3Br(Pipd)_2$	4310	4740	5180			6540		9710	23260sh	25000		
$CuCl_2Br_2(Pipd)_2$	4310	4740	5180			6290		9520	17240sh	21050		
$CuBr_4(Pipd)_2$						5810		9170	16530sh	18700	23260sh	28570
$CuCl_3$ · Morph	4280	4700	5130	5810sh	6670		12500		19230	24700sh		
$CuCl_4(Morph)_2$	4310	4700	5150	5780sh	6670		12200		22730sh	26320		
$CuCl_3Br(Morph)_2$	4330	4700	5150	5880sh	6670		12350		22730sh	25970		
$CuCl_2Br_2(Morph)_2$	4330	4760sh	5180sh			6900		10100	16670sh	21280		
$CuBr_4(Morph)_2$	4310sh	4760sh				6670		10000	16400sh	18870	27780	

[1] The positions of these bands in the complexes and in the ligands (Morph · HX or Pipd · HX, 4290–310, 4640–720, 5130–50, 5680–810, 6620–70, 8230–330 cm^{-1}) do not change on deuteration, while on heating the band at 5130–80 cm^{-1} in the complexes and in the ligands dissappear.

band, thus accounting for its weak absorbance (6–8). The weakness is justified, being this band polarized parallel to the Cu–Cu direction of the dimers (6) and only the crystals having such and orientation may contribute to its absorption. A short-polymeric (dimeric?) nature of the $CuCl_3^3$ · L complexes may be proposed on the basis of their crystalline nature, melting point not too much greater than those of the other complexes, and great solubility.

No thermocromic behaviour of the solid complexes is observed in the 290–370°K temperature range.

The geometry of the CuX_4^{2-} species in the solid state depends on many factors, including crystal field stabilization, ligand-ligand repulsion, Jahn-Teller distortions, hydrogen bonding and van der Waals forces.

The important role of hydrogen bonding, prevailing over the ligand size effect, is illustrated by examining the electronic spectra of our CuX_4^{2-}, CuX_3Y^{2-}, $CuX_2Y_2^{2-}$ and CuY_4^{2-} (X = Cl and Y = Br) complexes (Table II), where the cations have similar dimensions. For the bis morpholinium copper-tetrachloride and trichloridemonobromide the electronic spectra suggest an approaching square-planar configuration (5,6), which indicates the prevailing effect of the crystal field stabilization, since extensive NH · · · Cl hydrogen bonding reduces the effective charge on the chlorine atoms (9,10). In all the other bis morpholinium systems, the electronic spectra (Table II) suggest the presence of distorted tetrahedral species as the result of the prevailing ligand-ligand repulsion, which offset the crystal field stabilization (9,10), by the diminished hydrogen bonding possibility, as the number of the Cl ions decreases (or for an increase in the disorder of the hydrogen bonding (3)). These effects may also be responsible for the distorted tetrahedral configuration of all the bis piperidiniumcopper tetrahalide species.

A tendency to form hydrogen bonding is recognized in the morpholinium cation greater than in in the piperidinium cation. This is also supported by the red shift of the d-d band (10870 cm^{-1}) of the $CuCl_3$ · Pipd with respect to the d-d band position (12500 cm^{-1}) of the $CuCl_3$ · Morph indicating a distortion toward tetrahedral geometry.

Exemplifying spectra are reported in Figure 1.

The prevalent role of the NH · · · Cl hydrogen bonding in causing the planar geometry is confirmed by the electronic spectra of the complexes in EtOH or DMF solution, which show a single maximum with a broad tail extending to lower energy at 11000 and 9100 cm^{-1} respectively. The abatement of the NH · · · Cl hydrogen bonding by effect of the solvents

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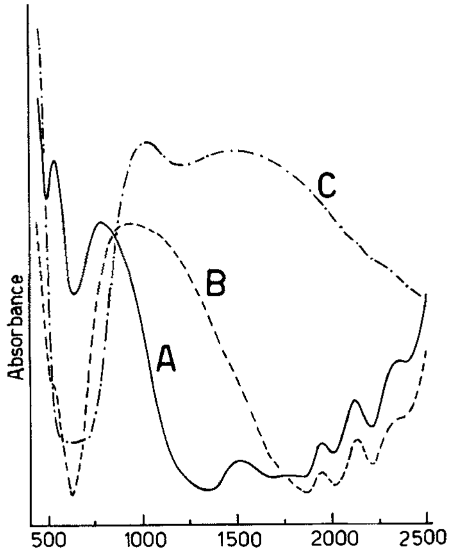

FIGURE 1 Exemplifying d–d spectra of complexes with an approaching square-planar geometry ($CuCl_3$ · Morph, $CuCl_4(Morph)_2$ and $CuCl_3Br(Morph)_2$) (A), with a distorted tetrahedral geometry ($CuCl_2Br_2(Morph)_2$, $CuBr_4(Morph)_2$ and $CuX_mY_n(Pipd)_2$ ($m = 2, 3, 4; n = 1, 2, 4; m + n = 4$)) (C) and with intermediate type (A) and (C) geometry ($CuCl_3$ · Pipd) (B).

and the axial solvent perturbations, insufficient to create planarity (11), restore also in the $CuCl_3$ · L, $CuCl_4(Morph)_2$ and $CuCl_3Br(Morph)_2$ complexes the distorted tetrahedral geometry. In EtOH or DMF solution (Table I) the $CuCl_3$ · L complexes act as uni-univalent electrolytes and the tetrahalo-cuprates as di-univalent electrolytes (12). The increasing conductivities in the order $CuCl_4^{2-} < CuCl_3Br^{2-} < CuCl_2Br_2^{2-} < CuBr_4^{2-}$, particularly in DMF solution, may be due to a decreasing outer coordination-sphere association between the amine cations and the copper tetrahalide anions.

The room-temperature magnetic moments of the solid complexes agree well with the proposed configurations (13,14). The complexes containing the bromide ion have magnetic moments lower than those containing an increasing number of chloride ions, indicating a greater tendency for antiferromagnetic coupling to occur in copper bromide than in copper chloride complexes (15).

Far-infrared Spectra

The far-i.r. spectra for the complexes and the appropriate starting amine hydrohalide salts are listed and assigned in Table III. The frequencies of the ν(Cu–Cl)

TABLE III

Far-infrared spectra (600–60 cm^{-1}) of the hydrohalide salts and their tetrahalo-and mixed-tetrahalo-cuprates

	ν(CuCl)			ν(CuBr)		δ(CuX)			Lattice	Other far i.r. bands
Pipd · HCl										552s 433s 395ms 283vs 164vsb 101ms 69m
Pipd · HBr										546s 428s 392ms 275vs 130vsb 81ms
$CuCl_3$ · Pipd	287vs	265sh	237m			174m	148ms		100w 74w	531s 420s 382ms 206w
$CuCl_4(Pipd)_2$	302vs	280vs				160s	140sh		100wb	540s 421s 394m 252sh 235w
$CuCl_3Br(Pipd)_2$	300sh	288vsb		230m	200wb	152s	128sh		93wb	542s 523s 391m 250m
$CuCl_2Br_2(Pipd)_2$	298sh	280vsb		210m		162w	150m	125mb	80w	537vs 421s 388m 250m
$CuBr_4(Pipd)_2$				236ms	212ms	167m	112mb		80w	540vs 422s 387m 248sh
Morph · HCl										592m 432s 410s 278ms 258m 140vsb 93ms 73m
Morph · HBr										586m 426s 403s 267ms 254m 129msb 70m
$CuCl_3$ · Morph	313sh	298vs	236vw			182sh			74m	582m 432s 412s 278sh 165s 120ms
$CuCl_4(Morph)_2$	295vs					181m			77m	580m 430s 401s 264sh 150s
$CuCl_3Br(Morph)_2$	294vs	278sh		230mb		177m	118w		76m	578m 430s 410s 142sb
$CuCl_2Br_2(Morph)_2$	300sh	284vs		226m	191w	174m	133ms		66m	570m 422s 401s 266sh 150m
$CuBr_4(Morph)_2$				230vs		175sh	134s		95m 67w	570m 422s 401s 268w 155m

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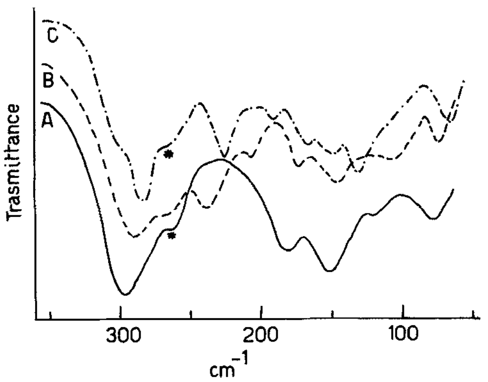

FIGURE 2 Exemplifying far-i.r. spectra of complexes with an approaching square-planar geometry as $CuCl_4(Morph)_2$ (A), with a distorted tetrahedral geometry as $CuCl_2Br_2(Morph)_2$ (C) and with intermediate type (A) and (C) geometry as $CuCl_3 \cdot Pipd$ (B).
*Ligand band.

modes in the complexes with approaching square-planar geometry are significantly different from those found in complexes with a distorted tetrahedral geometry. The principal Cu–Cl absorption band appears at 294–298 cm^{-1} in the former and at 280–288 cm^{-1} in the latter (Figure 2). The band at 302 cm^{-1} in the $CuCl_4(Pipd)_2$ complex may arise from a distortion in this complex stronger than in the other or from the presence of approaching square-planar configuration unities (10).

In the $Cu_2Cl_6^{2-}$ spectra the bands at 265 and 236–7 cm^{-1} could be bridging ν(Cu–Cl) (16).

The assignments of the Cu–X modes reported in Table II are made by comparison with the spectra of copper halides of known structure (16–18).

The multiplicity of the Cu–X bands is indicative of distortion from regular T_d or D_{4h} symmetry. In fact the triply degenerate t_2 mode in T_d symmetry splits into an e and b_2 mode, both stretching modes, in D_{2d} symmetry and into an e_u and a_{2u} (out-of-plane bending) in D_{4h} symmetry (10). Also the degeneracy of the e mode in D_{4h} symmetry is removed when the geometry becomes D_{2h} (or lower) in the b_{2u} and b_{3u} modes (10).

Hydrogen Bonding

In the parent amine hydrohalides a complex series of absorptions are found at 2600–2800 (very strong) and 2400–2500 (strong) cm^{-1}, which became attenuated on deuteration, indicating that an N–H motion is involved (19). The positions of these bands are in agreement with the other secondary amine hydrochlorides (19, 20).

In the $CuCl_3 \cdot L$, $CuCl_4^{2-}$ and $CuCl_3Br^{2-}$ bis morpholinium complexes, with an approaching square-planar configuration, these bands are shifted to 3110–20 and 3030–40 cm^{-1} (two well-resolved bands, which are also attenuated on deuteration) implying a strong N–H bond as electron density is removed from NH · · · Cl interaction and into the CuCl bond (8). In the distorted tetrahedral complexes of piperidinium and morpholinium cations one strong and broad band appears at 3070 cm^{-1} in the former and two strong and broad bands at 3085–95 and 3020–25 cm^{-1} in the latter.

Also the bending N–H mode at 1575–85 and 1550–65 cm^{-1} in piperidinium and morpholinium hydrohalides, respectively, which disappears on deuteration reapparing at 1200–1300 cm^{-1}, is sensitive to the CuX_4^{2-} geometry, being shifted to higher energies (1570–1580 cm^{-1}) in the complexes which approach square-planar configuration. In the distorted tetrahedral complexes this band remains stationary or is lowered in energy (1560–75 cm^{-1} in the piperidinium complexes and 1550 cm^{-1} in the morpholinium complexes).

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